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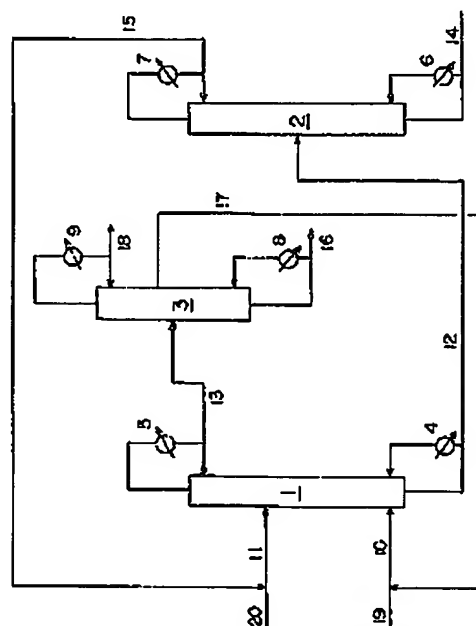
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(54) 【発明の名称】 ジアリアルカーボネートの連続的製造方法

(57) 【要約】

【課題】 高い反応収率、選択率およびエネルギー効率で、連続的にジアリアルカーボネートを製造する方法を提供する。

【解決手段】 2基の反応蒸留塔を用いて、触媒の存在下、ジアルキルカーボネートと芳香族ヒドロキシ化合物とを反応させて、アルキルアリアルカーボネートを生成させ、さらに、アルキルアリアルカーボネートからジアリアルカーボネートを連続的に製造する際に、第1反応蒸留塔の塔上部から、副生する脂肪族アルコール及びアルキルアリアルエーテルを未反応のジアルキルカーボネートと共に溜出させ、これを中間溜分抜き出し段のある蒸留塔に供給して精留し、中間溜分抜き出し段から抜き出したジアルキルカーボネートを主体とする中間溜分を第1反応蒸留塔に供給して再利用する。



## PATENT ABSTRACTS OF JAPAN

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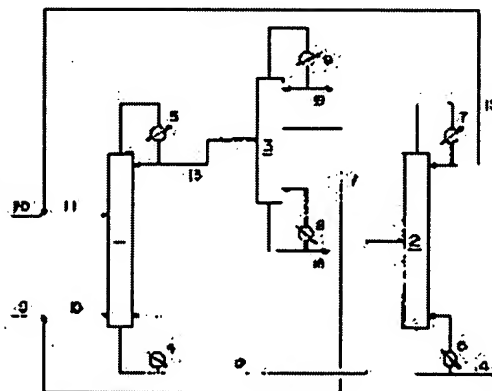
TANAKA TATSURO

## (54) CONTINUOUS PRODUCTION OF DIARYLCARBONATE

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for continuously producing a diarylcarbonate in high reaction yield, selectivity and energy efficiency.

SOLUTION: A method for continuously producing a diaryl carbonate comprises reacting a diarylcarbonate with an aromatic hydroxy compound in the presence of a catalyst by the use of two reaction distillation towers, and subsequently producing the diarylcarbonate from the obtained alkylarylcarbonate. Therein, the by-produced aliphatic alcohol, the alkylarylether and the unreacted dialkylcarbonate are together distilled out from the tip of the first reaction distillation tower, charged into a distillation tower having an intermediate fraction-discharging stage, finely distilled, and subsequently subjected to the discharge of an intermediate fraction consisting mainly of the dialkylcarbonate from the intermediate fraction-discharging stage. The discharged intermediate fraction is charged into the first reaction distillation tower for its reutilization.



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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the diaryl carbonate by the ester exchange reaction. In more detail, dialkyl carbonate and an aromatic series hydroxy compound are made to react under existence of a catalyst, alkyl aryl carbonate is generated, and it is further related with the approach of manufacturing diaryl carbonate continuously from alkyl aryl carbonate. As various chemistry raw materials, diaryl carbonate is a compound especially useful as the raw material and intermediate field of a polycarbonate.

[0002]

[Description of the Prior Art] Diaryl carbonate and an aromatic series hydroxy compound are made to react, alkyl aryl carbonate and manufacturing diaryl carbonate or those mixture further are known well, and these reactions are expressed with a degree type.

$(RO) 2CO + ArOH \rightarrow (RO) (ArO) CO + ROH$  (1)  $(RO) (ArO) CO + ArOH \rightarrow 2(ArO) CO + ROH$  (2) -- or --  $2(RO) (ArO) CO \rightarrow 2(ArO) CO + (RO) 2CO$  (3) (R shows an aliphatic series radical or an alicycle group machine among a formula, and Ar shows an aromatic series radical.)

However, these reactions are static reaction and it is known that especially the reaction of a formula (1) and a formula (2) inclines toward the Hara system very greatly. Moreover, generally the rate of reaction was also slow, therefore by these reactions, in order to have manufactured diaryl carbonate efficiently to alkyl aryl carbonate and a pan, it was accompanied by great difficulty.

[0003] The rate of reaction was raised, and efficiently, alkyl aryl carbonate and in order to manufacture diaryl carbonate further, the examination using a reaction distilling column of the manufacture approach was made. And, performing the reaction of dialkyl carbonate and an aromatic series hydroxy compound in the 1st column, and making the disproportionation of alkyl aryl carbonate perform in the 2nd column using two sets of reaction distilling columns, respectively The light fraction containing the alcohol which carries out a byproduction, or unreacted dialkyl carbonate is extracted from the 1st and 2nd reaction distilling-column upper part, respectively. The light fraction containing the dialkyl carbonate extracted from the 2nd reaction distilling-column upper part is circulated to the 1st reaction distilling column. The heavy fraction containing the alkyl aryl carbonate extracted from the lower part is supplied to the 2nd reaction distilling column. the 1st reaction circulation -- a column -- Consist of extracting the heavy fraction which contains diaryl carbonate from the 2nd reaction distilling-column lower part. The continuous manufacture approach of the diaryl carbonate from dialkyl carbonate and an aromatic series hydroxy compound is proposed (JP,4-211038,A and JP,4-235951,A).

[0004] By the way, as mentioned above, the above-mentioned reaction must distill off to a limit the fatty alcohol and the unreacted dialkyl carbonate which carry out a byproduction in the 1st and 2nd reaction distilling column by the conventional approach, respectively, in order to

obtain diaryl carbonate by high yield, since it inclines toward the Hara system very extremely in balanced theory. in order to fully distill off the fatty alcohol which exists in the 1st reaction distilling-column upper part so much -- a column -- the amount of draws from the upper part is made to increase, and the approach of distilling off fatty alcohol with unreacted dialkyl carbonate is adopted. However, although it is not indicated at all by two above-mentioned patents (JP,4-211038,A and JP,4-235951,A), since dialkyl carbonate is a reaction raw material in the 1st reaction distilling column, it is necessary to supply the dialkyl carbonate containing the fatty alcohol distilled out of the 1st reaction distilling column to the 1st reaction distilling column, and to reuse it as a reaction raw material, after separating fatty alcohol. Generally the dialkyl carbonate containing fatty alcohol is supplied to a distilling column (following and fatty alcohol separation column), fatty alcohol is distilled out of this distilling-column upper part, dialkyl carbonate is extracted from this distilling-column lower part, and it recycles in the 1st reaction distilling column.

[0005] however, fatty alcohol separation -- a column -- when the dialkyl carbonate extracted from the lower part was recycled in the 1st reaction distilling column and used continuously, the reacting weight of the both sides of the reaction of the dialkyl carbonate in the 1st column and an aromatic series hydroxy compound and the disproportionation of the alkyl aryl carbonate in the 2nd column fell gradually, and un-arranging [ which cannot maintain the volume of predetermined diaryl carbonate ] arose. the place which considered various the cause -- two sets of reaction distilling columns, and fatty alcohol separation -- it became clear that it was because the inactive byproduction alkyl aryl ether is accumulated in the reaction of above-mentioned both sides between columns.

[0006] Although [ according to the approach of two above-mentioned patents (JP,4-211038,A and JP,4-235951,A) ] there is almost no byproduction of the alkyl aryl ether by side reaction, according to our examination, it turned out that the alkyl aryl ether of a considerable amount generates. Although the alkyl aryl ether cannot be extracted from the 2nd reaction distilling-column lower part, is extracted from this reaction distilling-column upper part and it circulates through it from those physical properties to the 1st distilling column, that part is distilled from this reaction distilling-column upper part with the alkyl aryl ether with which the alkyl aryl ether through which it circulated to this 1st reaction distilling column is generated in the 1st reaction distilling column. however, this alkyl aryl ether -- fatty alcohol and dialkyl carbonate -- the above-mentioned fatty alcohol separation -- when a column is supplied, from this distillation tub upper part, this alkyl aryl ether cannot be extracted and is recycled by the 1st reaction distilling column with dialkyl carbonate. namely, the alkyl aryl ether which carries out a byproduction -- two sets of reaction distilling columns, and fatty alcohol separation -- between columns, it will circulate mutually and will accumulate as a result. If are recording of the alkyl aryl ether progresses, the concentration of a reaction component will fall, a reaction rate will become slow, and it will become impossible to maintain a predetermined volume. furthermore, two sets of reaction distilling columns and fatty alcohol separation -- it is great loss of energy that a lot of unnecessary components circulate between columns.

[0007] the approach of making dialkyl carbonate and an aromatic series hydroxy compound reacting under existence of a catalyst, making alkyl aryl carbonate generating using two sets of reaction distilling columns, and manufacturing diaryl carbonate continuously from alkyl aryl carbonate further as mentioned above -- two sets of reaction distilling columns, and fatty alcohol separation, between columns, since the alkyl aryl ether is accumulated, it cannot react efficiently and is not satisfactory as a industrial approach.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention makes dialkyl carbonate and an aromatic series hydroxy compound react under existence of a catalyst, makes alkyl aryl carbonate generate using two sets of reaction distilling columns, does not

have further the fault described above as an approach of manufacturing diaryl carbonate from alkyl aryl carbonate, are high reaction yield, selectivity, and energy efficiency, and is to offer the approach of manufacturing diaryl carbonate continuously.

[0009]

[Means for Solving the Problem] this invention persons use two sets of reaction distilling columns, as a result of repeating examination wholeheartedly for solution of the above-mentioned problem. In the approach of making dialkyl carbonate and an aromatic series hydroxy compound reacting under existence of a catalyst, making alkyl aryl carbonate generating, and manufacturing diaryl carbonate continuously from alkyl aryl carbonate The fatty alcohol which was extracted from the upper part of the 1st reaction distilling column and which carried out the byproduction, The light fraction containing the alkyl aryl ether and dialkyl carbonate Rectified by having introduced into the distilling column with a middle-cut draw stage continuously, extracted fatty alcohol from the distilling-column upper part, and the alkyl aryl ether was extracted from the distilling-column lower part. By extracting the fraction which mainly consists of dialkyl carbonate from a middle-cut draw stage, and supplying this to the 1st reaction distilling column continuously Pressing down loss of dialkyl carbonate required for a reaction to the minimum The fatty alcohol which carries out a byproduction in the 1st and 2nd reaction distilling column is removed. And the thing for which are recording into the 1st and 2nd reaction distilling column of the alkyl aryl ether is suppressed Since the fatty alcohol which it is [ fatty alcohol ] possible and biases a reaction balance toward the Hara system in this case falls to a limit and does not accumulate the alkyl aryl ether, either, without requiring a great installation cost A balance is also advantageous, and a reaction rate is also quick, and it finds out that diaryl carbonate manufacture can be continuously carried out in high reaction yield, high selectivity, and high energy efficiency since there is also no loss of energy, and came to complete this invention.

[0010] this invention -- the bottom of existence of a catalyst, and the 1st reaction distilling column -- setting -- a column, distilling a light fraction out of the upper part Dialkyl carbonate and an aromatic series hydroxy compound are made to react, and the reaction mixture containing alkyl aryl carbonate is collected from a bottom. Subsequently the dialkyl carbonate which this reaction mixture is made to react further and carries out a byproduction in the 2nd reaction distilling column under existence of a catalyst -- a column, distilling out of the upper part and recycling in the 1st reaction distilling column In the continuous manufacture approach of diaryl carbonate of collecting the reaction mixture containing diaryl carbonate from a bottom the column of the 1st reaction distilling column -- by making the fatty alcohol and the alkyl aryl ether which carry out a byproduction distill with unreacted dialkyl carbonate, supplying this to a distilling column with a middle-cut draw stage, and rectifying it from the upper part While collecting fatty alcohol from this distilling-column upper part and collecting the alkyl aryl ether from this distilling-column lower part on the other hand It is the continuous manufacture approach of the diaryl carbonate characterized by extracting the middle cut which makes dialkyl carbonate a subject from a middle-cut draw stage, supplying this middle cut to the 1st reaction distilling column, and reusing it.

[0011]

[Embodiment of the Invention] The dialkyl carbonate which is the reaction raw material of this invention is expressed with the following formula (4).

$R_1OCO$  two  $R_2$  (4) ( $R_1$  and  $R_2$  show the alkyl group of carbon numbers 1-10, the alkenyl radical of carbon numbers 2-10, the cycloalkyl radical of carbon numbers 5-10, or the aralkyl radical of carbon numbers 7-12 among a formula, and even if  $R_2$  are the same as  $R_1$  respectively, they may differ.)

Specifically, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate, diaryl carbonate, dihexyl carbonate, dioctyl carbonate, dicyclohexyl carbonate, dibenzyl

carbonate, methylethyl carbonate, ethylene carbonate, propylene carbonate, etc. are mentioned. Especially the things used preferably are dimethyl carbonate and diethyl carbonate in these.

[0012] The aromatic series hydroxy compound which is another reaction raw material of this invention approach is expressed with a formula (5).

ArOH (5) (Ar shows the aromatic series radical of carbon numbers 1-20 among a formula.)

Specifically, a phenol, o-, m- or p-cresol, o-, m- or p-ethylphenol, o-, m- or p-propyl phenol, o-, m- or p-methoxy phenol, 2, 6-dimethylphenol, 2, 4-dimethylphenol, 3, 4-dimethylphenol, o-, m- or p-chlorophenol, 1-naphthol, 2-naphthol, etc. are mentioned. Especially a desirable thing is a phenol in these.

[0013] The alkyl aryl carbonate said by this invention is expressed with a formula (6).

R<sub>3</sub>OCOOAr (6) (Ar expresses the same thing as a formula (5) among a formula.) Moreover, R<sub>3</sub> expresses the same thing as R<sub>1</sub> or R<sub>2</sub> in a formula (4).

There are specifically methylphenyl carbonate, ethyl phenyl carbonate, propyl phenyl carbonate, buthylphenyl carbonate, and alkylphenyl carbonate like hexyl phenyl carbonate, and methyl or ethyl tolyl carbonate, methyl or ethyl xylyl carbonate, methyl, or ethyl chlorophenol is mentioned further. Especially desirable things are methylphenyl carbonate and ethyl phenyl carbonate in these.

[0014] The diaryl carbonate furthermore said by this invention is expressed with a formula (7).

(ArO)<sub>2</sub>CO (7) (Ar shows the same thing as a formula (5) among a formula.)

Specifically, diphenyl carbonate, JITORIRU carbonate, JIKISHIRIRU carbonate, dinaphthyl carbonate, dichlorophenyl carbonate, etc. are mentioned. In this, especially a desirable thing is diphenyl carbonate.

[0015] Anythings can be used for it if the catalyst used by this invention promotes the ester exchange reaction of dialkyl carbonate or alkyl aryl carbonate, and an aromatic series hydroxy compound, and the disproportionation of alkyl aryl carbonate. For example Bu<sub>2</sub>SnO, Ph<sub>2</sub>SnO, 2SnO, Bu<sub>2</sub>Sn (C<sub>8</sub>H<sub>17</sub>)<sub>2</sub>, Bu<sub>2</sub>Sn (OPh)<sub>2</sub>, Bu<sub>2</sub>Sn (OCH<sub>3</sub>) (OEt) lead compound; AlX(s)<sub>3</sub>, such as tin compound-bO(s), such as 2 and Bu<sub>2</sub>Sn(OPh)O(OPh) SnBu<sub>2</sub>, and Pb (OPh)<sub>2</sub>, Pb (OCOCH<sub>3</sub>)<sub>2</sub>, TiX<sub>3</sub>, TiX<sub>4</sub>, ZnX<sub>2</sub>, FeX<sub>3</sub> and SnX<sub>4</sub>, and VX<sub>5</sub> grade (here -- X -- a halogen --) an acetoxyl group, an alkoxyl group, and an aryloxy group are shown. It is mentioned. As an example AlCl<sub>3</sub>, aluminum 3 TiCl<sub>4</sub>, Ti (OPh)<sub>4</sub> Ti (OPh)<sub>4</sub> Ti (OEt) (OPr) copper compounds (here -- acac -- aceti acetone complex ligand --), such as 4, Lewis acid compound; Zr (acac)<sub>4</sub> of Ti(Obu)<sub>4</sub> grade, zirconium compound; CuCl of ZrO<sub>2</sub> grade, CuCl<sub>2</sub>, CuBr, and CuBr<sub>2</sub>, CuI, CuI<sub>2</sub>, Cu (OAc)<sub>2</sub> It is mentioned that Ac shows an acetyl group etc. Especially a desirable thing is a tin compound or a titanium compound especially.

[0016] As two sets of reaction distilling columns used by this invention, the number of stages of distillation may be two or more (a real stage or theoretical plate) steps, and as long as it is the distilling column in which continuous distillation is possible, what kind of thing may be used. a reaction -- a column -- it mainly happens in the inner liquid phase section. You may be any of a distilling column which have the tray tower which used various trays, the packed column filled up with various packing or a plate part, and a packing fraction as such a distilling column.

[0017] By the approach of this invention, a raw material can be supplied to the stage of the arbitration of the 1st reaction distilling column from \*\*\*\* eclipse \*\*\*\*\* of arbitration. Raw materials may be any of the mixture of liquid, a steam, or a liquid and a steam. An aromatic series hydroxy compound and dialkyl carbonate are supplied to the 1st reaction distilling column as a catalyst and a reaction raw material. Although especially the mole ratio of dialkyl carbonate to the aromatic series hydroxy compound to supply is not limited, it is usually the range of 0.1-20, and both need to exist by substantial concentration in the 1st reaction distilling column. And in the 1st reaction distilling column, from dialkyl carbonate and aromatic series carbonate, the byproduction of the fatty alcohol is carried out and alkyl aryl carbonate mainly

generates by the reaction according to the reaction formula of the above (1).

[0018] In the 1st reaction distilling column, although the light fraction containing fatty alcohol, the alkyl aryl ether, alkyl carbonate, etc. which carry out a byproduction can be extracted from the stage of arbitration other than a bottom, the concentration of fatty alcohol and the alkyl aryl ether is usually as high as the upper part of a column. Therefore, as for the light fraction containing fatty alcohol, the alkyl aryl ether, dialkyl carbonate, etc. which carry out a byproduction, extracting from the overhead is more desirable. The presentations of this light fraction are usually 5 - 20 % of the weight of fatty alcohol, 80 - 95 % of the weight of dialkyl carbonate, and 0.1 or less % of the weight of alkyl aryl ether.

[0019] In the 1st reaction distilling column, the heavy fraction containing the generated alkyl aryl carbonate is especially extracted from the lower part of a distilling column continuously [ it is desirable and ] in the state of the liquid phase from a bottom. A catalyst is also included in this heavy fraction and the 2nd reaction distilling column is supplied as it is. The presentations of this heavy fraction are usually 20 - 50 % of the weight of dialkyl carbonate, 1 or less % of the weight of alkyl aryl ether, 20 - 50 % of the weight of aromatic series hydroxy compounds, 10 - 40 % of the weight of alkyl aryl carbonate, and 1 or less % of the weight of catalysts.

[0020] By the approach of this invention, the heavy fraction containing the generated alkyl aryl carbonate which was continuously extracted in the state of the liquid phase from the raw material, i.e., the 1st reaction distilling-column lower part, can be supplied to the stage of the arbitration of the 2nd reaction distilling column from \*\*\*\* eclipse \*\*\*\*\* of arbitration. The catalyst is also included in this heavy fraction. In case the 2nd reaction distilling column is supplied, raw materials may be any of the mixture of liquid, a steam, or a liquid and a steam.

[0021] In the 2nd reaction distilling column, from alkyl aryl carbonate, the byproduction of the dialkyl carbonate is carried out and diaryl carbonate mainly generates by the reaction according to the reaction formula of the above (3). Generally, the above-mentioned (2) formula has a remarkably disadvantageous balance compared with the above-mentioned (3) formula, and the reaction according to (3) types usually occurs dominantly in the 2nd reaction distilling column. Therefore, in order that the inside of the 2nd reaction distilling column may make a balance advantageous, few [ as much as possible ] things of dialkyl carbonate are desirable. Since the concentration of dialkyl carbonate is very low in the 2nd reaction distilling-column lower part according to the approach of this invention although both evaporation of a reaction and a light fraction progresses when the heavy fraction containing the catalyst from the 1st reaction distilling-column lower part, alkyl aryl carbonate, and dialkyl carbonate is supplied to the 2nd reaction distilling column, the reaction according to the reaction formula of the above (3) occurs efficiently advantageously.

[0022] In the 2nd reaction distilling column, although the light fraction containing the dialkyl carbonate which carried out the byproduction, the alkyl aryl ether, etc. can be extracted from the stage of arbitration other than a bottom, the concentration of dialkyl carbonate and the alkyl aryl ether is usually as high as the upper part of a column. Therefore, as for the light fraction containing the dialkyl carbonate which carried out the byproduction, the alkyl aryl ether, etc., extracting from the overhead is more desirable. The presentations of this light fraction are usually 40 - 60 % of the weight of dialkyl carbonate, 1 or less % of the weight of alkyl aryl ether, and 40 - 60 % of the weight of aromatic series hydroxy compounds. Since dialkyl carbonate is a reaction raw material, the 1st reaction distilling column is made to supply and carry out the reuse of the light fraction containing the dialkyl carbonate which carried out the byproduction, the alkyl aryl ether, etc. extracted continuously from the upper part of the 2nd reaction distilling column in the 1st reaction distilling column.

[0023] In the 2nd reaction distilling column, the heavy fraction containing the generated diaryl carbonate is especially extracted from the distilling-column lower part continuously [ it is desirable and ] in the state of the liquid phase from a bottom. The presentations of this heavy



fraction are usually 5 - 15 % of the weight of aromatic series hydroxy compounds, 5 - 15 % of the weight of alkyl aryl carbonate, 70 - 90 % of the weight of diaryl carbonate, and 5 or less % of the weight of catalysts. Components other than diaryl carbonate in this liquid phase, i.e., an aromatic series hydroxy compound, alkyl aryl carbonate, a catalyst, etc. are removed by conventional methods well known to these contractors, such as distillation, and diaryl carbonate with few impurities is obtained. The removed aromatic series hydroxy compound, alkyl aryl carbonate, a catalyst, etc. are supplied to the 1st or 2nd reaction distilling column, and a reuse is carried out. An aromatic series hydroxy compound and a catalyst are preferably supplied to the 1st reaction distilling column, and, on the other hand, alkyl aryl carbonate is preferably supplied to the 2nd reaction distilling column.

[0024] The general operating condition of the 1st and 2nd reaction distilling column in this invention is as follows. 50-300 degrees C whenever [ reaction distilling-column internal temperature ] is 100-250 degrees C preferably. A reaction rate improves so that whenever [ reaction distilling-column internal temperature ] is high, but since it is in the inclination which by-products, such as the alkyl aryl ether, increase, it is not desirable to make it not much high. Although the pressure in a reaction distilling column changes also with the class of reaction raw material to be used, the structure of the plate of a distilling column, and classes of packing, it can usually be performed under the pressurization of the range of 10 - 3000kP\*\* thru/or reduced pressure. As especially desirable range, it is 40-2000kP. Although the mean flow-time of the liquid phase in a reaction distilling column is based also on other operating conditions, it is 0.3 - 10 hours preferably for 0.1 to 20 hours, respectively. a reflux ratio -- usually -- 0-10 -- 0-5 are used more preferably.

[0025] It dissolves in reaction raw materials, such as for example, an aromatic series hydroxy compound, and a catalyst is usually first supplied to the 1st reaction distilling column. After removing those light fractions enough in generating light fractions, such as alcohol and water, in case a catalyst is dissolved in a reaction raw material, it is desirable to supply the 1st reaction distilling column. The approach which this contractor usually uses is employable, such as using the mixing vessel which attached the distilling column to the tub upper part, for example as batch process catalyst dissolver as an approach of removing those light fractions. According to this approach, a catalyst and the reaction raw material of for example, an aromatic series hydroxy compound are taught to the catalyst dissolver which attached the distilling column to the upper part, a catalyst is dissolved with churning and heating, and light fractions, such as generated alcohol and water, are removable [ suppressing loss of a reaction raw material to the minimum ] out of a system with the distilling column of the tub upper part. Since a catalyst exists in the liquid phase, it flows into the 2nd reaction distilling column one by one from the lower part of the 1st reaction distilling column. the reaction raw material supplied to the 1st reaction distilling column as an amount of catalysts used -- receiving -- 0.00001-10-mol % -- it is 0.0001-5-mol % preferably. If too few, a reaction rate will become inadequate, and when many [ too ], there is an inclination which the amounts of byproductions, such as the alkyl aryl ether, increase.

[0026] In this invention approach, it is important to rectify the light fraction containing fatty alcohol, the alkyl aryl ether, dialkyl carbonate, etc. which were extracted from the upper part of the 1st reaction distilling column and which carried out the byproduction using a distilling column with a middle-cut draw stage. The number of stages of distillation may be two or more (a real stage or theoretical plate) steps, it may have a middle-cut draw stage, and as long as continuous distillation is possible for the distilling column with a middle-cut draw stage, what kind of thing is sufficient as it. You may be any of a distilling column which have the tray tower which used various trays, the packed column filled up with various packing or a plate part, and a packing fraction as such a distilling column.

[0027] The light fraction containing fatty alcohol, the alkyl aryl ether, dialkyl carbonate, etc.

which were extracted from the 1st reaction distilling-column upper part and which carried out the byproduction can be supplied from the inlet of the number of the arbitration of the stage of arbitration of a distilling column with a middle-cut draw stage. In case it supplies, these light fractions may be any of the mixture of liquid, a steam, or a liquid and a steam.

[0028] although the light fraction containing fatty alcohol can be extracted from the stage of arbitration other than a bottom in a distilling column with a middle-cut draw stage -- the concentration of fatty alcohol -- usually -- a column -- the upper part is high. Therefore, as for the light fraction containing fatty alcohol, extracting from the overhead is more desirable. The presentations of this light fraction are usually 40 - 60 % of the weight of fatty alcohol, and 40 - 60 % of the weight of dialkyl carbonate.

[0029] although the heavy fraction containing the alkyl aryl ether can be extracted from the stage of the arbitration of the distilling-column lower part in a distilling column with a middle-cut draw stage -- the concentration of the alkyl aryl ether -- usually -- a column -- the lower part is high. Therefore, as for the heavy fraction containing the alkyl aryl ether, extracting from a bottom is more desirable. The presentations of this heavy fraction are usually 70 - 90 % of the weight of dialkyl carbonate, and 10 - 30 % of the weight of alkyl aryl ether.

[0030] In a distilling column with a middle-cut draw stage, the middle cut which mainly consists of dialkyl carbonate is extracted from the middle-cut draw stage between the draw stage of the light fraction containing fatty alcohol, and the draw stage of the heavy fraction containing the alkyl aryl ether. The middle-cut draw stage where the fatty alcohol in the extracted middle cut and the concentration of the alkyl aryl ether serve as the minimum according to other operating conditions of a distilling column is chosen more preferably. The part or all is continuously supplied to the extracted middle cut which mainly consists of dialkyl carbonate by the 1st distilling column.

[0031] By the distilling column with the middle-cut draw stage mentioned above, suppressing loss of dialkyl carbonate required for a reaction to the minimum, the fatty alcohol which biases toward the Hara system the reaction balance which carries out a byproduction in the 1st and 2nd reaction distilling column is reduced to a limit, and it becomes possible to suppress are recording into the 1st and 2nd reaction distilling column of the alkyl aryl ether, without requiring a great installation cost.

[0032] The general operating condition of a distilling column with the middle-cut draw stage in this invention is as follows. 50-250 degrees C whenever [ distilling-column internal temperature ] is 50-300 degrees C preferably. Although the pressure in a distilling column changes also with the class of reaction raw material to be used, the structure of the plate of a distilling column, and classes of packing, it can usually be performed under the pressurization of the range of 10 - 2000kP\*\* thru/or reduced pressure. As especially desirable range, it is 50-1000kP. a reflux ratio -- usually -- 0-15 -- 0-10 are used more preferably.

[0033] In this invention, although it is not necessary to necessarily use a solvent, ether, aliphatic hydrocarbon, and aromatic hydrocarbon can be used for a reaction as an inactive solvent.

[0034]

[Example] An example is shown below and this invention is concretely explained to it.

The equipment containing the catalyst dissolver which attached the distilling column to the example (adjustment of catalyst) tub upper part was used. Catalyst dissolution equipment is a mixing vessel with a glass jacket with a full capacity of 1l. the column where the distilling column was filled up with the coil pack made from stainless steel (diameter of 2.5mm) as packing -- it was 0.3m of quantities, and the distilling column of 4cm of tower diameters, and a capacitor, a liquid-liquid separation machine, and draw tubing have been arranged to the overhead, and the interconnecting tube with catalyst dissolver has been arranged to the bottom. Phenol 545g and dibutyltin oxide 136g were taught to catalyst dissolver, respectively,

at first, carrying out total reflux, under the ordinary pressure condition, it agitated and whenever [ catalyst dissolver internal temperature ] was gradually raised in the overhead section of a distilling column to 150 degrees C. Then, while raising whenever [ catalyst dissolver internal temperature ] from 150 degrees C to 180 degrees C over about 5 hours, keeping the temperature of a liquid-liquid separation machine at 40 degrees C, the aqueous phase (water/phenol = 10 weight sections / 1 weight section) produced with the liquid-liquid separation vessel was extracted out of the system from draw tubing, and the phenol phase flowed back to the distilling column. Consequently, the distillate of a phenol was suppressed as much as possible (phenol distillate ratio = 0.2% pair preparation), and 671g of catalyst (moisture = 0.03%)-phenol solutions which hardly contain moisture was obtained from catalyst dissolver.

[0035] (Manufacture of diphenyl carbonate) A series of equipments including two reaction distilling columns (1), and (2) and a distilling column (3) shown in drawing 1 were used. the column where the reaction distilling column (1) was filled up with the coil pack made from stainless steel (diameter of 2.5mm) as packing -- it was 1m of quantities, and the distilling column of 4cm of tower diameters, and from the bottom, the conduit (11) has been arranged in the location of 0.5m of upper parts from the conduit (10) and the bottom, and the reboiler (4) and the conduit (12) have be arranged to the overhead in the location of 0.05m of upper parts at the capacitor (5), the conduit (13), and the bottom. the column where the reaction distilling column (2) was filled up with the coil pack made from stainless steel (diameter of 2.5mm) as packing -- it was 2m of quantities, and the distilling column of 4cm of tower diameters, and the conduit (12) has been arranged in the location of 0.75m of upper parts from the bottom, and the reboiler (6) and the conduit (14) have been arranged to the overhead at the capacitor (7), the conduit (15), and the bottom. the column where the distilling column (3) was filled up with the coil pack made from stainless steel (diameter of 2.5mm) as packing -- it was 1.5m of quantities, and the distilling column of 4cm of tower diameters, and the conduit (13) has been arranged in the location of 0.5m of upper parts from the bottom, and middle draw tubing (17) has be arranged from the reboiler (8), the conduit (16), and the bottom to the overhead in the location of 0.75m of upper parts at the capacitor (9), the conduit (18), and the bottom.

[0036] From the conduit (20), the phenol and the catalyst-phenol solution (at amount of supply = the time of 10.3g-solution/) obtained by the above-mentioned catalyst preparation actuation were supplied, it combined with the component of the amount of draws (15), and the reaction raw material was continuously supplied to the reaction distilling column (1) from the conduit (11). Furthermore, from the conduit (19), dimethyl carbonate was supplied, it combined with the component of middle draw tubing (17), and the reaction raw material was continuously supplied to the reaction distilling column (1) from the conduit (10). Maintaining the thermal stress in a reaction distilling column (1) at a predetermined value, it extracted generation liquid from the bottom more nearly continuously than a conduit (12), and acquired the liquid phase containing methylphenyl carbonate. On the other hand, the mixture which contains a methanol, dimethyl carbonate, and an anisole from the overhead more nearly continuously than a conduit (13) was extracted. The liquid phase containing the methylphenyl carbonate extracted from the conduit (12) was supplied to the reaction distilling column (2). Maintaining the thermal stress in the reaction distilling column 2 at a predetermined value, it extracted generation liquid from the bottom more nearly continuously than a conduit (14), and acquired the liquid phase containing diphenyl carbonate. On the other hand, the mixture which contains a methanol, dimethyl carbonate, and an anisole more nearly continuously than a conduit (15) was extracted from the overhead, and it recycled in the reaction distilling column (1) through the conduit (11). The mixture containing the methanol and dimethyl carbonate which were extracted from the conduit (13), and an anisole was supplied to the distilling column (3). Maintaining at a predetermined value, from the overhead, from the conduit (18), the thermal stress in a distilling column (3)

condensed the methanol, extracted it continuously, from the bottom, from the conduit (16), condensed the anisole and extracted it continuously. Furthermore, from middle draw tubing (17), the dimethyl carbonate which hardly contains a methanol and an anisole was extracted, and it recycled through the conduit (10) in the reaction distilling column (1).

[0037] The flow rate of the service condition of the reaction distilling column at the time of a steady state (1) and (2), and a distilling column (3) and the component in tubing was shown in Table 1 and 2, respectively. Reaction results were shown in Table 4 and 5.

[0038] The dimethyl carbonate containing an anisole was extracted from the conduit (16) from the bottom of this distilling column, without extracting a middle cut from the example (manufacture of diphenyl carbonate) distilling column of a comparison (3), and the same operation as an example 1 was performed except having changed the process flow of drawing 1 so that a reaction distilling column (1) might be made to recycle through a conduit (10). The flow rate of the service condition of a reaction distilling column (1) and (2), and a distilling column (3) and the component in tubing was shown in Table 1 and 3, respectively. Reaction results were shown in Table 4 and 5. About the example of a comparison, the data of the time of a start and ten days after were shown.

[0039]

[Table 1]

表 1

	第 1 反応蒸留塔			第 2 反応蒸留塔			蒸留塔 (3)		
	塔底温度 (℃)	塔頂圧力 (atm)	還流比 —	塔底温度 (℃)	塔頂圧力 (atm)	還流比 —	塔底温度 (℃)	塔頂圧力 (atm)	還流比 —
実施例 (定常状態)	215	6.5	0.4	190	0.2	0.4	105	1.5	7
比較例 (スタート時)	215	6.5	0.4	190	0.2	0.4	100	1.5	7
(10日後)	216	6.5	0.4	193	0.2	0.4	100	1.5	7

[0040]

[Table 2]

表2 実施例（定常状態）

管番号	管内の流体流量 (g/時)										
	10	11	12	13	14	15	16	17	18	19	20
成分											
メタノール	2.6	0.5	0.5	33.3	—	0.5	—	2.6	30.7	—	—
ジメチルカーボネート	598.3	401.7	366.1	550.9	0.2	401.7	1.7	519.7	29.5	78.6	—
アニソール	—	4.4	4.3	0.3	—	4.4	0.3	—	—	—	—
フェノール	—	400	309.7	—	15.8	295.1	—	—	—	—	113.4
メチルフェニルカーボネート	—	0.3	134.8	—	16.2	0.3	—	—	—	—	—
ジフェニルカーボネート	—	—	7.7	—	89.3	—	—	—	—	—	—
触媒	—	3.6	3.6	—	3.6	—	—	—	—	—	3.6

[0041]

[Table 3]

表3 比較例（スタート時と10日後）

管番号	管内の流体流量 (g/時)									
	10	11	12	13	14	15	16	18	19	20
成分										
メタノール										
（スタート時）	2.6	0.5	0.5	33.3	—	0.5	2.6	30.8	—	—
（10日後）	2.3	0.4	0.4	29.5	—	0.4	2.3	27.2	—	—
ジメチルカーボネート										
（スタート時）	600.5	401.7	367.1	551	0.2	401.7	520	31.3	78.8	—
（10日後）	646.8	353.2	324.4	602	0.2	353.2	575.9	26.1	72.7	—
アニソール										
（スタート時）	—	0.3	0.2	—	—	0.3	—	—	—	—
（10日後）	5	69.8	70	5	—	70.1	5	—	—	—
フェノール										
（スタート時）	—	401	308.5	—	15.2	296.3	—	—	—	114.5
（10日後）	—	400	320	—	12.8	308.2	—	—	—	100.3
メチルフェニルカーボネート										
（スタート時）	—	0.3	135.5	—	15.5	0.3	—	—	—	—
（10日後）	—	0.3	119.4	—	23.6	0.3	—	—	—	—
ジフェニルカーボネート										
（スタート時）	—	—	7.7	—	89.5	—	—	—	—	—
（10日後）	—	—	6.8	—	72.6	—	—	—	—	—
触媒										
（スタート時）	—	3.6	3.6	—	3.6	—	—	—	—	3.6
（10日後）	—	3.6	3.6	—	3.6	—	—	—	—	3.6

[0042]

[Table 4]

表4 第1反応蒸留塔の反応成績

	フェノールの転化率 (重量%)	メチルフェニルカーボネートの 生成速度 (g/時)
実施例 (定常状態)	22.6	134.5
比較例 (スタート時)	22.7	135.2
(10日後)	19.9	119.1

[0043]

[Table 5]

表5 第2反応蒸留塔の反応成績

	メチルフェニルカーボネートの 転化率 (重量%)	ジフェニルカーボネートの 生成速度 (g/時)
実施例 (定常状態)	87.8	81.6
比較例 (スタート時)	87.8	81.8
(10日後)	79.9	65.8

[0044]

[Effect of the Invention] The fatty alcohol which was extracted from the 1st reaction distilling-column upper part according to the approach of this invention and which carried out the byproduction, The light fraction containing the alkyl aryl ether, dialkyl carbonate, etc. Introduce into a distilling column with a middle-cut draw stage continuously, and it rectifies in this distilling column. The heavy fraction which extracts the light fraction containing fatty alcohol continuously from the distilling-column upper part, and contains the alkyl aryl ether The middle cut which extracted continuously from the distilling-column lower part, and was extracted from the middle-cut draw stage and which mainly consists of dialkyl carbonate The part or all by supplying the 1st reaction distilling column continuously Suppressing loss of dialkyl carbonate required for a reaction to the minimum The fatty alcohol which biases toward the Hara system the reaction balance which carries out a byproduction in the 1st and 2nd reaction distilling column is reduced to a limit. Since the fatty alcohol which it is [ fatty alcohol ] possible and biases a reaction balance toward the Hara system is falling to a limit, without suppressing are recording into the 1st and 2nd reaction distilling column of the alkyl aryl ether requiring a great installation cost, Even if it does not enlarge the 1st reaction distilling column superfluously, since sufficient reaction capacity is securable, diaryl carbonate can be efficiently manufactured continuously with high reaction yield and high selectivity by the comparatively small installation cost to alkyl aryl carbonate and a pan.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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CLAIMS

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[Claim(s)]

[Claim 1] Distilling a light fraction out of the upper part, dialkyl carbonate and an aromatic series hydroxy compound are made to react, and the reaction mixture containing alkyl aryl carbonate is collected from a bottom. the bottom of existence of a catalyst, and the 1st reaction distilling column -- setting -- a column -- subsequently the dialkyl carbonate which this reaction mixture is made to react further and carries out a byproduction in the 2nd reaction distilling column under existence of a catalyst -- a column, distilling out of the upper part and recycling in the 1st reaction distilling column In the continuous manufacture approach of diaryl carbonate of collecting the reaction mixture containing diaryl carbonate from a bottom the column of the 1st reaction distilling column -- by making the fatty alcohol and the alkyl aryl ether which carry out a byproduction distill with unreacted dialkyl carbonate, supplying this to a distilling column with a middle-cut draw stage, and rectifying it from the upper part While collecting fatty alcohol from this distilling-column upper part and collecting the alkyl aryl ether from this distilling-column lower part on the other hand The continuous manufacture approach of the diaryl carbonate characterized by extracting the middle cut which makes dialkyl carbonate a subject from a middle-cut draw stage, supplying this middle cut to the 1st reaction distilling column, and reusing it.

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[Translation done.]